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Michael J. Fluss, Brian D. Wirth, Mark Wall, Thomas E. Felter, Maria J. Caturla, Alison Kubota, Tomas Diaz de la Rubia

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Defect based spin mediation in δ-phase plutonium

Michael J. Fluss, Brian D. Wirth, Mark Wall, Thomas E. Felter, Maria J. Caturla, Alison Kubota, and Tomas. Diaz de la Rubia
Chemistry and Materials Science Directorate
Lawrence Livermore National Laboratory,
P.O. Box 808 East Avenue,
Livermore, CA, USA 94577, U.S.A.

ABSTRACT

We earlier reported the measured decrease of electrical resistivity during isochronal-annealing of ion irradiation damage that was accumulated at low-temperature (10 or 20K), and the temperature dependence of the resistance of defect-populations produced by low-temperature damage-accumulation and annealing in a stabilized δ-phase plutonium alloy, Pu(3.3 at%Ga)[1]. We noted that the temperature dependence of the resistance of defects resulting from low-temperature damage accumulation and subsequent annealing exhibits a *-ln(T)* temperature dependence suggestive of a Kondo impurity. A discussion of a possible "structure-property" effect, as it might relate to the nature of the δ-phase of Pu, is presented.

INTRODUCTION

It has recently been shown, through an analysis of magnetic susceptibility and electrical resistivity data of δ-stabilized plutonium [2], that the hypothesis of a Kondo effect [3] (T_K~200-300K) in δ-plutonium is extant, thus implying that 5f electrons are localized as in the case of other known concentrated Kondo systems. However, although explaining the origin of the anomalous resistivity in δ-stabilized Pu(Al), the first principles origin of the "stabilized" or the pure fcc Pu δ-phase remains as an unsolved problem. Recent theoretical work [4], based on dynamical mean field theory (DMFT), suggests that the δ-phase and the α-phase of plutonium are two sides of the f-electron delocalization-localization knife-edge, total energies differing by only a few 10^{ths} of an eV. In this picture, the α-phase is not a weakly correlated phase; it is just slightly on the delocalized side of the localization-delocalization transition. Here, the δ-phase is intrinsically stable while the alloy-stabilized fcc binary alloys (e.g., Pu(Al) or Pu(Ga)) are the consequence of a "destabilization" of the α-phase by small amounts of impurities. In this presentation we will suggest a new related mechanism of defect based spin mediation stabilization of the pure Pu δ-phase due to *equilibrium* vacancies, predicated on our discovery of Kondo-like impurity behavior for *non-equilibrium* vacancies in δ-phase Pu(Ga).

EXPERIMENTAL DETAILS

We report on the restively measured isochronal annealing $\Delta\rho$ ˜ . ρ_0 and temperature dependence of the resistivity, ρ . of annealed defect populations resulting from low-temperature (10K to 20K) accumulated ion-damage in the stabilized fcc delta-Pu(3.3 at%Ga) (figure 1). Isochronal annealing curves from damage accumulation of self-irradiation (the α decay of plutonium) and from 3.8MeV proton irradiations were measured and compared with combined molecular-dynamics and kinetic-Monte-Carlo simulations (MD-KMC). As a result, we discovered a strong inverse temperature dependence of the resistance of specific defect populations that we produced by damage accumulation and subsequent *partial* annealing at 150 and 250K.

The similarity in the characteristics of the annealed vacancy population for self-irradiation and proton irradiation in the specimen was surprising. The vacancy defect population is shown in figure 2 for three annealing temperatures. This analysis is a result of the MD-KMS calculations that best describe the annealing data in figure 1.

Damage populations resulting from low-temperature (10K) damage-accumulation were annealed at specific temperatures 30,150 and 250K producing intermediate *defect populations*. The temperature dependence of the resistance, . . was measured by invoking Matthiesson's rule [5]. Hence, the defect resistance was measured by subtracting the measured resistance of the defected specimen minus the resistance of the same specimen in the fully annealed state as a function of temperature. Of course, experimental corrections were required to account for damage accumulated from self-irradiation during the measurements. The specific resistivity of the defects in the 150K and 250K populations was found to vary by a factor of ~8 over the temperature range 150 to 10K. Referring to the MD-KMC modeling in figure 2, indicates that the defect populations at 150K and 250K are described primarily as vacancy and small vacancy clusters.

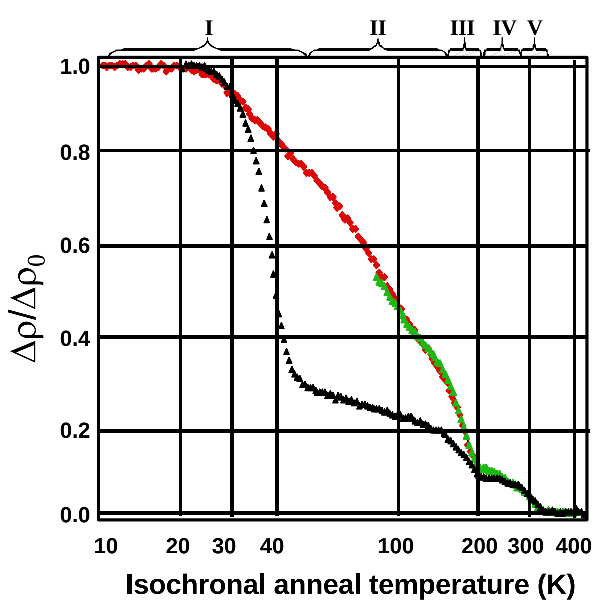

Figure 1. Normalized isochronal annealing data for three Pu(Ga) damage-accumulation experiments. The red and green points (upper) are for 3.8 MeV proton irradiations and the (lower) black points are from a self-irradiation from an average 5.05 MeV alpha decay of Pu. The approximate boundaries of the five annealing stages are indicated above.

The temperature dependence, Ṛ ̣ of these vacancy dominated defect populations (150K and 250K) follows a Ṛ□̣ = -a*ln*(T)+b dependence which can be seen for the data in figure 3, and share a common *ln*(T) intercept, all of which is suggestive of a Kondo-like magnetic impurity at vacancy defect sites. We note, a systematic deviation from a linear fit is observed in the vicinity of T=10K suggesting that the energy scale or Kondo temperature is T_K<10K for vacancies and small vacancy clusters in δ-phase PuGa.

DISCUSSION

The consequences of this observation could be profound. It suggests that the implied 5f localization in the neighborhood of vacancies, and possibly other dilations in the lattice, results in localized magnetic behavior with a low Kondo temperature T_K<10K compared to that determined earlier for bulk δ-phase PuAl of T_K~200-300K, the later suggesting an intermediate-valence system [2]. The question then is; is this the origin of reduced metallic bonding? Might this be the structure-property relationship or *impurity* that precipitates a more global electronic structure change leading to the "stabilization" of the delta-phase, as suggested by Cooper and co-workers [6]?

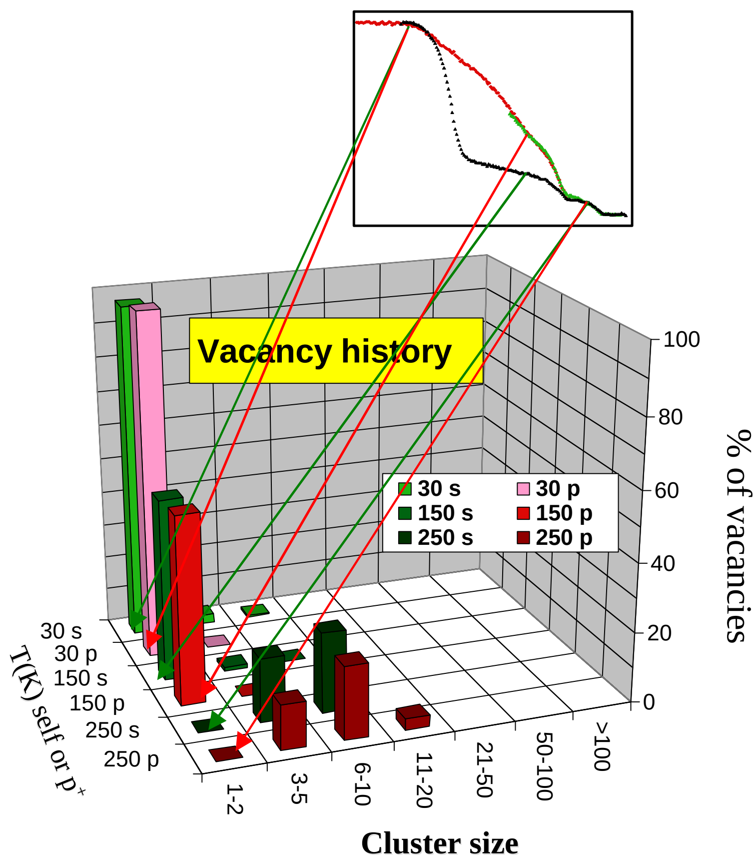

Figure 2. The surviving vacancy population from a 10K soak followed by annealing at three temperatures, 30, 150, and 250K for either self-irradiation (s) or proton irradiation (p). The data is parsed into cluster sizes. What is striking and unexpected is the similarity of the vacancy defect populations between the two very different types of irradiation.

It is interesting to note that plutonium exhibits excessive relaxation about Ga sites in δ-phase Pu(1 wt% Ga) [7]. While the Ga is found by EXAFS to be substitutional in the fcc lattice, first neighbor Pu atoms are observed to be 3.7% contracted and second nearest neighbors are 0.9% contracted. An estimate for this “free volume” between first and second neighbors is about 1/3rd the volume of a lattice vacancy. Qualitatively this points to the possibility that the physics leading to Kondo-like behavior of stabilized alloy may be related to the Kondo properties of non-equilibrium vacancies described above, and this speculation is consistent with the trend in T_K as well.

Given the above, we posit the following structure-property mechanism for the stabilization of pure Pu in the δ-phase. The transition to the δ-phase commences at T=593K, while the melting point for Pu is 913K. At 2/3rd the melting point we estimate an equilibrium vacancy population of at least ~10^{-4}. Indeed, given the low value of the EXAFS Debye-Waller factor measured for Pu-Pu bonds in stabilized δ-PuGa [8], a higher concentration of vacancies (a lower formation enthalpy) might even be expected. Thus, it is reasonable, but remains to be proven, that a small concentration of equilibrium vacancies gives rise to the local spin-sites (Kondo impurities) that stabilize the δ–phase of pure plutonium.

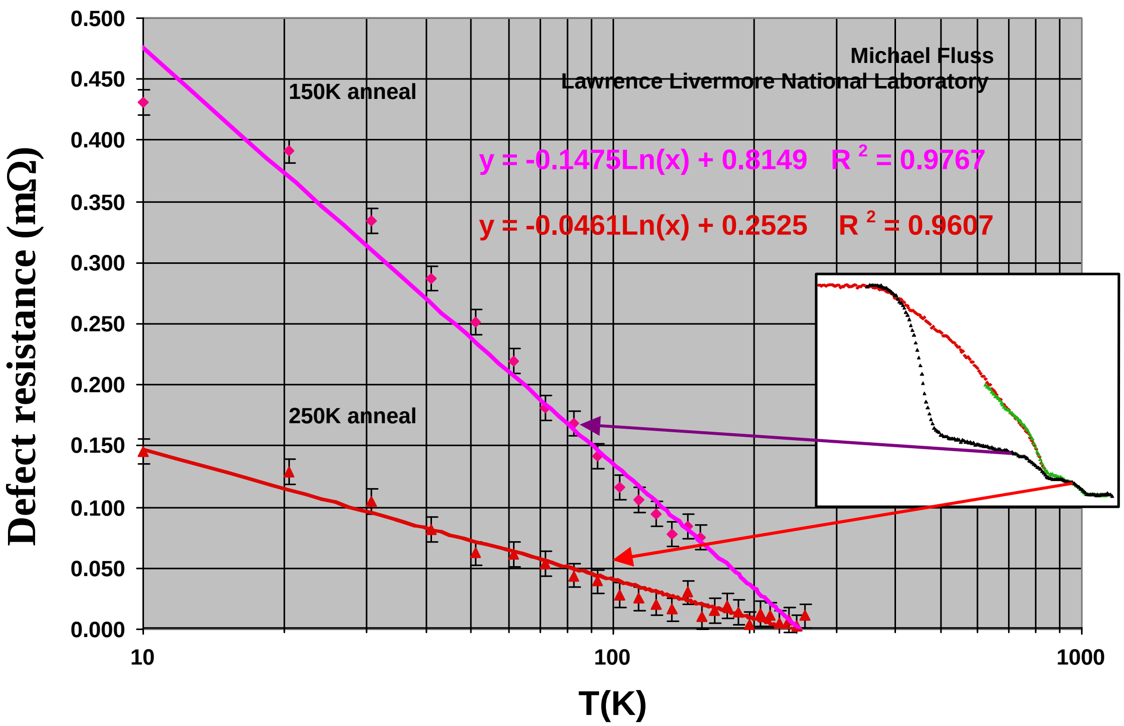

Figure 3. The temperature dependence of two different defect populations are shown. The upper set of points is for damage accumulated at 10K from self-irradiation and then annealed at 150K. The temperature dependence for the second defect population is shown in the lower points and was a result of annealing, in turn, at 250K. Note that the form of a Kondo impurity is given by $\rho_{spin}= c\rho_M\,[1+ (3zJ)\ln T/\varepsilon_F]$ where c = *concentration*, z = *coordination number*, J = exchange energy, . ρ_M = *strength of exchange scattering.*

CONCLUSIONS

The low temperature phase diagram of plutonium and its compounds may very well hold the answer to the origins of the many conflicting anomalies exhibited by Pu. Recent work [9,10] has contributed more knowledge about the unusual and exceptional nature of the ground state properties of Pu and the possible existence of a quantum singularity at T=0K. Continued experimental progress, although challenging, should be well worth the effort. Making direct experimental contact with isolated spins and local moments extant in Pu and Pu compounds will be an important objective of future work.

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